

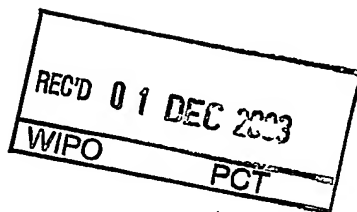


PCT/EP 0 3 / 1 2 2 2 0



INVESTOR IN PEOPLE

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

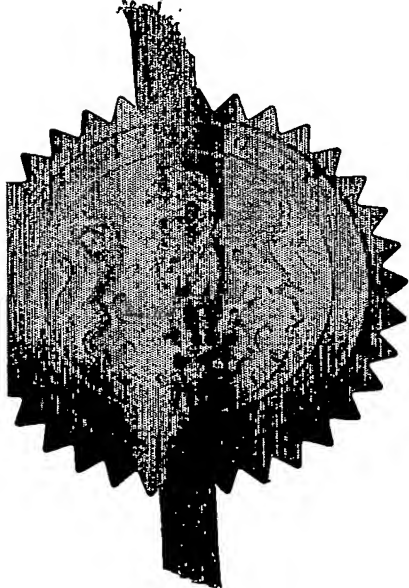


I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed R. Mahon  
Dated 9 October 2003

BEST AVAILABLE COPY

**PRIORITY  
DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

The  
Patent  
Office



11DEC02 E770177-5 002898  
P01/7700 0.00-0228877.7

The Patent Office

Cardiff Road  
Newport  
Gwent NP10 8QQ

**Request for grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference J3674 (C)/rkk

---

2. Patent application number 0228877.7  
(The Patent Office will fill in this part) 11 DEC 2002

---

3. Full name, address and postcode of the or of each applicant (*underline all surnames*) UNILEVER PLC  
UNILEVER HOUSE, BLACKFRIARS  
LONDON, EC4P 4BQ  
  
 Patents ADP number (*if you know it*) 50426956002  
  
 If the applicant is a corporate body, give the country/state of its incorporation UNITED KINGDOM

---

4. Title of the invention SHAMPOO COMPOSITIONS

---

5. Name of your agent (*if you have one*) ELLIOTT Peter William  
  
 "Address for Service" in the United Kingdom to which all correspondence should be sent (*including the postcode*) PATENT DEPARTMENT, UNILEVER PLC  
COLWORTH HOUSE, SHARNBROOK  
BEDFORD, MK44 1LQ  
  
 Patents ADP number (*if you know it*) 6573927001 *IS*

---

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (*if you know it*) the or each application number
 

	Country	Priority application number ( <i>if you know it</i> )	Date of filing (day / month / year)

---

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application
 

	Number of earlier application	Date of filing (day/month/year)

---

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (*Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d))

YES

# Patents Form 1/77

9 Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

## Continuation sheets of this form

Description

27

Claim(s)

4

Abstract

1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

## Priority Documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature(s)



Date: 10/12/02

Sandra Jane EDWARDS, Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Ravinder K Kundra, Tel 01234 22 2439

## Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

DUPLICATE

- 1 -

SHAMPOO COMPOSITIONSTechnical Field

5 The invention is concerned with rinse-off hair-conditioning compositions which are applied to the hair and then substantially rinsed away. It is particularly concerned with hair shampoo compositions, which both clean the hair and provide conditioning benefit to the hair. More  
10 specifically, it is concerned with improving the deposition of silicone conditioning oil onto the tip region of hair relative to the root region, from shampoo compositions which contain dispersed hydrophobic conditioning oil droplets and which are substantially free of cationic deposition  
15 polymers.

Background and Prior Art

Compositions which provide a combination of cleansing and  
20 conditioning to the hair are well known in the art. Such shampoo or shower-gel compositions typically comprise one or more surfactants for shampooing or cleansing purposes and one or more conditioning agents. The purpose of the conditioning agent is to make the hair easier to comb when  
25 wet and more manageable when dry, e.g. less static and fly-away. Typically, these conditioning agents are water-insoluble oily materials, cationic polymers or cationic surfactants.

30 Amongst the most popular conditioning agents used in shampoo products are oily materials such as mineral oils, naturally

---

occurring oils such as triglycerides and silicone polymers. These are generally present in the shampoo as dispersed hydrophobic emulsion droplets. Conditioning is achieved by the oily material being deposited onto the hair resulting in the formation of a film.

Conditioning compositions which provide conditioning only, without cleansing surfactants, are also well known in the art. Such compositions are generally applied to the hair after the cleansing composition has been rinsed away.

One method to improve deposition of conditioning oils onto hair is to use large droplets of oil. This method relies on physical contact between the hair and the droplets followed by the oil droplet wetting the hair surface and spreading.

Natural oils secreted by the sebaceous gland at the base of the hair lead to hair being more hydrophobic near the root rather than near the tip. This means that droplets deposited onto hair by the use of large droplets of oil are more likely to spread and form films on the hair at the base of the hair rather than near the tip of the hair, and this is found in practice.

Another method to enhance deposition of the conditioning oil droplets onto the hair is to employ a cationic deposition polymer in the composition. The use of such polymers is well known in the prior art.

The use of cationic polymers means that the oil droplets are flocculated with the cationic polymer on dilution of the

---

shampoo when the hair is rinsed. This leads to indiscriminate deposition of the cationic polymer, conditioning oil and any other insoluble materials onto the hair. The presence of extraneous materials in addition to the conditioning oil can lead to dulling of the appearance of the hair (loss of shine) and also to a heavy feel to the hair (because of the presence of the cationic polymer).

Certain consumers find the effects arising from the two deposition methods described above to be undesirable in that they lead to the hair feeling greasy at the roots or heavy and dull.

In attempts to overcome the problems in the prior art, it has been considered desirable to target the deposition of the conditioning oil droplets onto the tip regions of the hair in preference to the root regions, and much research has been carried out in this field of work. Although it would be desirable to make the surface of the oil droplets more hydrophilic, it had always been considered that the high levels of surfactant in shampoo compositions would dominate the surface chemistry and hydrophilicity of the oil droplets. Thus the conventional view is that irrespective of and additives added to the conditioning oil droplets, the shampoo surfactant would control the droplet hydrophilicity and deposition.

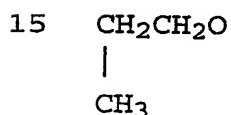
It has now surprisingly been found, that by blending certain types of surface active block copolymer with silicone conditioning oil emulsion droplets, enhanced deposition of the droplets onto the tip regions of hairs can be achieved.

Although not wishing to be bound by the scientific reasoning underlying this phenomenon, it seems that surface active polymer remains at the droplet surface, even in the presence of other surfactant molecules from the shampoo, making the

5 droplets more hydrophilic than the droplets in conventional oil droplet-containing shampoos. This leads to improved deposition of the droplets towards the more hydrophilic tip region of the hair.

10 Summary of the invention

In the following description, EO represents  $\text{CH}_2\text{CH}_2\text{O}$  and PO represents

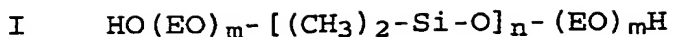


In a first aspect the invention provides an aqueous hair  
20 conditioning composition comprising:

a) from 1% to 50% by weight of a cleansing surfactant,

b) discrete, dispersed droplets comprising a water  
25 insoluble silicone conditioning oil, characterised in that the mean diameter of the droplets ( $D_{3,2}$ ) is from 2 to 100 micrometres and

c) a surface active block copolymer according to  
30 formula I:



wherein m is 30 or more, n is 5 or more and the ratio n/m is  
from 0.1 to 1.2.

5

#### Detailed Description

Compositions in accordance with the invention are formulated  
as compositions for the cleansing of hair and subsequent  
10 rinsing such as shampoos, cleansing mousses or shower gels.  
It is highly preferred that cleansing compositions according  
to the invention should contain less than 0.01% by weight of  
any cationic deposition polymer.

#### 15 Surface Active Polymer

A suitable surface active block copolymer for use in  
compositions according to the invention is a silicone-based  
block copolymer according to formula I above. Suitable  
20 silicone block copolymers for use in compositions according  
to the invention comprise from 50% to 85% by weight of  
polyethyleneoxide in the molecular formula, preferably 60%  
to 85%. Suitable silicone block copolymers have a molecular  
weight of 3000 unified mass units or more, preferably 3500  
25 or more, more preferably 4000 or more.

In formula I, the degree of polymerisation, m, is indicated  
as the same for each polyethyleneoxide block. For the sake  
of clarity, it should be explained that these degrees of  
30 polymerisation are mean values and are approximately the

---



same rather than identical. This is a result of the polymerisation methods used for production of the compounds.

Suitably surface active block copolymers for the invention  
5 are according to formula I



wherein m is 30 or more, preferably 35 or more, n is 5 or  
10 more, preferably 7 or more, more preferably 10 or more and  
wherein the ratio n/m is from 0.1 to 1.2, preferably from  
0.2 to 0.7.

Suitably, the level of surface active block copolymer is in  
15 the range from 0.01% to 0.4% by weight of the composition,  
preferably from 0.02% to 0.3%, more preferably from 0.04% to  
0.2%, even more preferably from 0.05% to 0.1%.

A suitable method for the preparation of these polymers is  
20 described in detail in a paper by J. Yang, G. Wegner and R  
Konigsfeld in "Colloid and Polymer Science" volume 270 pages  
1080 to 1084 (1992).

#### Silicone Conditioning Oil

25 An essential component of compositions according to the  
invention is hydrophobic silicone conditioning oil. In order  
for such an oil to exist in discrete droplets in the  
compositions according to the invention, it must be water-  
30 insoluble. By water-insoluble is meant that the solubility  
in water at 25°C is 0.01% by weight of water or less.

---

It is essential that the  $D_{3,2}$  average particle diameter of the hydrophobic conditioning oil droplets in the composition is 2 micrometres or more, preferably 5 micrometres or more, and more preferably 12 micrometres or more.. The average  
5 particle size of the oil droplets in the composition is 100 micrometres or less to prevent problems in stabilising the composition from separation of components.

Silicone  $D_{3,2}$  mean droplet diameter may be measured by means  
10 of a laser light scattering technique, for example using a 2600D Particle Sizer from Malvern Instruments.

The total amount of silicone conditioning oil present in the composition is preferably from 0.01% to 10 % by weight of  
15 the total composition more preferably from 0.3% to 5%, most preferably 0.5% to 3 %.

Suitable silicones for use as conditioning oils include polydiorganosiloxanes, in particular polydimethylsiloxanes  
20 which have the CTFA designation dimethicone. Also suitable for use compositions of the invention are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol.

25 It is preferred if the silicone oil also comprises a functionalised silicone other than the surface active block copolymer of the invention.

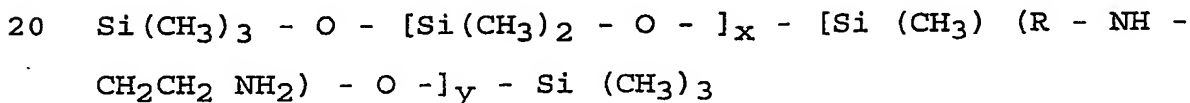
Suitable functionalised silicones include, for example,  
30 amino-, carboxy-, betaine-, quaternary ammonium-,

---

carbohydrate-, hydroxy- and alkoxy-substituted silicones. Preferably, the functionalised silicone contains multiple substitutions.

5 For the avoidance of doubt, as regards hydroxyl-substituted silicones, a polydimethylsiloxane merely having hydroxyl end groups (which have the CTFA designation dimethiconol) is not considered a functionalised silicone within the present invention. However, a polydimethylsiloxane having hydroxyl  
10 substitutions along the polymer chain is considered a functionalised silicone.

Preferred functionalised silicones are amino-functionalised silicones. Suitable amino functionalised silicones are  
15 described in EP 455,185 (Helene Curtis) and include trimethylsilylamodimethicone as depicted below, and are sufficiently water insoluble so as to be useful in compositions of the invention:



wherein  $x + y$  is a number from about 50 to about 500, and the weight percent amine functionality is in the range of  
25 from about 0.03% to about 8%, and wherein R is an alkylene group having from 2 to 5 carbon atoms. Preferably, the number  $x + y$  is in the range of from about 100 to about 300, and the weight percent amine functionality is in the range of from about 0.03% to 8%.

- 9 -

As expressed here, the weight percent amine functionality is measured by titrating a sample of the amino-functionalised silicone against alcoholic hydrochloric acid to the bromocresol green end point. The weight percent amine is  
5 calculated using a molecular weight of 45 (corresponding to  $\text{CH}_3\text{-CH}_2\text{-NH}_2$ ).

Suitably, the weight percent amine functionality measured and calculated in this way is in the range from 0.03% to 8%,  
10 preferably from 0.5% to 4%.

An example of a commercially available amino-functionalised silicone useful in the silicone component of the composition of the invention is DC-8566 available from Dow Corning.

15

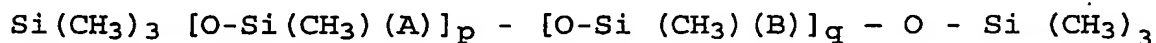
By "amino functional silicone" is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group. Examples of suitable amino functional silicones include: polysiloxanes having the  
20 CTFA designation "amodimethicone". Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC-8220, DC-8166, DC-8466, and DC-8950-114 (all ex Dow Corning), and GE 1149-75, (ex General Electric Silicones). Suitable quaternary silicone  
25 polymers are described in EP-A-0 530 974. A preferred quaternary silicone polymer is K3474, ex Goldschmidt.

Another preferred functional silicone for use as a component in the hydrophobic conditioning oil is an alkoxy-substituted  
30 silicone. Such molecules are known as silicone copolyols

---

and have one or more polyethyleneoxide or polypropyleneoxide groups bonded to the silicone polymer backbone, optionally through an alkyl linking group.

- 5 A non-limiting example of a type of silicone copolyol useful in compositions of the invention has a molecular structure according to the formula depicted below:



10

In this formula, A is an alkylene chain with from 1 to 22 carbon atoms, preferably 4 to 18, more preferably 10 to 16.

B is a group with the structure:  $-(\text{R})-(\text{EO})_r(\text{PO})_s-\text{OH}$  wherein R is a linking group, preferably an alkylene group with 1

- 15 to 3 carbon atoms. Preferably R is  $-(\text{CH}_2)_2-$ . The mean values of r and s are 5 or more, preferably 10 or more, more preferably 15 or more. It is preferred if the mean values of r and s are 100 or less. In the formula, the value of p is suitably 10 or more, preferably 20 or more, more  
20 preferably 50 or more and most preferably 100 or more. The value of q is suitably from 1 to 20 wherein the ratio p/q is preferably 10 or more, more preferably 20 or more. The value of p + q is a number from 11 to 500, preferably from 50 to 300.

25

Suitable silicone copolyols for use in compositions according to the invention have an HLB of 10 or less, preferably 7 or less, more preferably 4 or less. A suitable silicone copolyol material is DC5200, known as lauryl  
30 dimethicone copolyol, available from Dow Corning.

Hydrophile/Lipophile balance or HLB is a well known parameter used by those skilled in the art to characterise surface active molecules and emulsifiers. Suitable methods for the experimental determination of HLB are in Griffin W.C, Journal of the Society of Cosmetic Chemists, volume 1 page 311 (1949).

It is preferred to use a combination of functional and non-functional silicones as the conditioning oil. Preferably these are blended into common droplets prior to incorporation into compositions according to the invention.

The viscosity of the silicone oil blend measured in isolation from the rest of the composition (i.e. not the viscosity of any pre-formed emulsion, but of the silicone blend forming the hydrophobic conditioning oil) is preferably in the range from  $5,000 \text{ mm}^2 \text{sec}^{-1}$  to  $1,000,000 \text{ mm}^2 \text{sec}^{-1}$  at  $25^\circ \text{C}$ . Suitable methods for measuring the viscosity of silicone oils are known to those skilled in the art, e.g. capillary viscometers. For high viscosity materials, a suitable method would be the use of a constant stress rheometer. Measurement of viscosity should be carried out at low shear rates where by the viscosity is independent of shear rate.

#### Cationic Deposition Polymer

A cationic deposition polymer is often used in hair treatment compositions, for enhancing conditioning performance. However this leads to problems arising from

the cationic polymer also remaining adhered to the hair, which can, in some cases, lead to a dirty, sticky feel to the hair some hours after use of the cleansing and conditioning composition for some consumers.

5

Such cationic polymers may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally be between 5 000 and 10 000 000 unified mass units, typically at least 10 000 and preferably in the range 100 000 to about 2 000 000. The polymers will have cationic, nitrogen-containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof.

It is highly preferred that compositions according to the invention should contain less than 0.04% by weight of such a cationic deposition polymer, more preferably less than 0.02%, even more preferably less than 0.01%. It is most preferred that such polymers are absent from the composition.

#### Preparation of Compositions

One method for preparing compositions according to the invention is to add a silicone conditioning oil, along with the other components comprising the hair treatment composition, followed by suitable mixing of the composition in order to ensure that the blend is dispersed as droplets of a suitable size.

15

However it is preferred if the hydrophobic silicone conditioning oil is first formed into an aqueous emulsion prior to incorporation into the hair treatment composition.

---

Thus another aspect of the invention is a method for preparing an aqueous hair conditioning composition comprising the steps of :

- 5           i)   preparing a solution comprising water and the surface active block copolymer,
- ii)   adding a silicone conditioning oil to said solution,
- 10          iii) forming the solution and the silicone conditioning oil into an oil-in-water emulsion by high-shear mixing,
- 15          iv) dispersing said oil-in-water emulsion comprising the block copolymer into a hair conditioning composition.

Another preferred method for preparing a hair conditioning composition according to the invention comprises the steps of:

- i)   preparing an oil-in-water emulsion of a silicone conditioning oil,
  - 25          ii) dispersing the surface active block copolymer into the emulsion,
  - iii) dispersing said oil-in-water emulsion comprising the block copolymer into a hair conditioning composition.
- 30
-



Suitable emulsifiers for use in the preparation of the aqueous emulsion are well known in the art and include anionic, cationic, zwitterionic, amphoteric and nonionic surfactants, and mixtures thereof. Examples of anionic surfactants used as emulsifiers for the silicone particles are alkylarylsulphonates, e.g., sodium dodecylbenzene sulphate, alkyl sulphates e.g., sodium lauryl sulphate, alkyl ether sulphates, e.g., sodium lauryl ether sulphate nEO, where n is from 1 to 20, alkylphenol ether sulphates, e.g., octylphenol ether sulphate nEO where n is from 1 to 20, and sulposuccinates, e.g., sodium dioctylsulposuccinate.

Examples of nonionic surfactants suitable for use as emulsifiers for the silicone droplets are alkylphenol ethoxylates, e.g., nonylphenol ethoxylate nEO, where n is from 1 to 50 and alcohol ethoxylates, e.g., lauryl alcohol nEO, where n is from 1 to 50, ester ethoxylates, e.g., polyoxyethylene monostearate where the number of oxyethylene units is from 1 to 30.

A preferred process for preparing oil-in-water emulsions of the mixed silicone droplets which can then be incorporated in the hair treatment compositions involves use of a mixer. Depending upon the viscosities of components of the silicone mixture a suitable mixer should be chosen so as to provide sufficient shear to give the required final particle size of the emulsion. Examples of suitable benchtop mixers spanning the range of necessary shear are Heidolph RZR2100, Silverson L4R, Ystral X10/20-750 and Rannie Mini-Lab 7.30VH high pressure homogeniser. Other mixers of similar specification

are well known to those skilled in the art and can also be used in this application. Equally it is possible to manufacture oil-in-water emulsions of this description on larger scale mixers which offer similar shear regimes to those described above.

It is preferred if the aqueous phase of the emulsion contains a polymeric thickening agent to prevent phase separation of the emulsion after preparation. Preferred thickening agents are cross-linked polyacrylates, cellulosic polymers or derivatives of cellulosic polymers.

Preferably, the mixer is also capable of having the temperature of mixing controlled, e.g. it comprises a jacket through which a heat transfer fluid can be circulated.

#### Cleansing Surfactant

Compositions according to the invention will comprise one or more cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair. Further surfactants may be present as an additional ingredient if sufficient for cleansing purposes is not provided by the emulsifier for the water-insoluble oily component. It is preferred that shampoo compositions of the invention comprise at least one further surfactant (in addition to any used as emulsifying agent for the silicone component) to provide a cleansing benefit.

Suitable cleansing surfactants, which may be used singularly or in combination, are selected from anionic, amphoteric and

zwitterionic surfactants, and mixtures thereof. The cleansing surfactant may be the same surfactant as the emulsifier, or may be different.

- 5 The total amount of cleansing surfactant (including any co-surfactant, and/or any emulsifier) in compositions of the invention is generally from 1 to 50, preferably from 2 to 40, more preferably from 10 to 25 percent by weight of the composition. For the sake of clarity, the surface active  
10 block copolymer is not here considered to be a cleansing surfactant.

#### Anionic Cleansing Surfactant

- 15 Shampoo compositions according to the invention will typically comprise one or more anionic cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair.
- 20 Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-  
25 olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may  
30 contain from 1 to 10 ethylene oxide or propylene oxide units, per molecule.
-

Typical anionic cleansing surfactants for use in shampoo compositions of the invention include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphate, triethanolamine dodecylbenzene sulphate, sodium cocoyl isethionate, sodium lauryl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, sodium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3), ammonium lauryl sulphate and ammonium lauryl ether sulphate(n)EO, (where n ranges from 1 to 3).

Mixtures of any of the foregoing anionic cleansing surfactants may also be suitable.

The total amount of anionic cleansing surfactant in shampoo compositions of the invention is generally from generally from 0.5 to 45, preferably from 1.5 to 35, more preferably from 5 to 20 percent by weight of the composition.

#### Co-surfactant

The composition can include co-surfactants, to help impart aesthetic, physical or cleansing properties to the composition.

A preferred example is an amphoteric or zwitterionic surfactant, which can be included in an amount ranging from 0 to about 8, preferably from 1 to 4 percent by weight.

Examples of amphoteric and zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl

betaines, alkyl sulphobetaines (sultaines), alkyl glycines, alkyl carboxyglycines, alkyl amphopropionates, alkylamphoglycines, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

10

Another preferred example is a nonionic surfactant, which can be included in an amount ranging from 0 to 8, preferably from 2 to 5 percent by weight of the composition.

15 For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic ( $C_8 - C_{18}$ ) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having  
20 from 6 to 30 ethylene oxide groups.

Other representative nonionic surfactants include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

25

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block  
30 of one or more glycosyl groups.

---

Preferred APGs are defined by the following formula:



wherein R is a branched or straight chain alkyl group which  
5 may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about C<sub>5</sub> to  
about C<sub>20</sub>. Preferably R represents a mean alkyl chain length  
of from about C<sub>8</sub> to about C<sub>12</sub>. Most preferably the value of R  
10 lies between about 9.5 and about 10.5. G may be selected  
from C<sub>5</sub> or C<sub>6</sub> monosaccharide residues, and is preferably a  
glucoside. G may be selected from the group comprising  
glucose, xylose, lactose, fructose, mannose and derivatives  
thereof. Preferably G is glucose.

15

The degree of polymerisation, n, may have a value of from  
about 1 to about 10 or more. Preferably, the value of n lies  
in the range of from about 1.1 to about 2. Most preferably  
the value of n lies in the range of from about 1.3 to about  
20 1.5.

25

Suitable alkyl polyglycosides for use in the invention are  
commercially available and include for example those  
materials identified as: Oramix NS10 ex Seppic; Plantaren  
1200 and Plantaren 2000 ex Henkel.

Other sugar-derived nonionic surfactants which can be  
included in compositions of the invention include the C<sub>10</sub>-C<sub>18</sub>

N-alkyl ( $C_1$ - $C_6$ ) polyhydroxy fatty acid amides, such as the  $C_{12}$ - $C_{18}$  N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy fatty acid amides, such as  $C_{10}$ - $C_{18}$  N-(3-methoxypropyl) glucamide.

The composition according to the invention can also optionally include one or more cationic co-surfactants included in an amount ranging from 0.01 to 10, more preferably from 0.05 to 5, most preferably from 0.05 to 2 percent by weight of the composition.

A preferred blend of surfactants comprises a mixture of ammonium lauryl ether sulfate, ammonium lauryl sulfates, PEG 5 cocamide and cocomide MEA (CTFA designations).

#### Suspending Agents

Optionally, the compositions according to the invention further comprise from 0.1 to 10 percent by weight, preferably from 0.6% to 6%, of a suspending agent. Suitable suspending agents are selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures

thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent, known as cross-linked polyacrylates, may also be used, they are available commercially as Carbopol 910; Carbopol 934, Carbopol 940, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing a monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trade mark) materials are available from Goodrich. The CTFA name for these materials is Carbomer.

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

#### Adjuvants

The compositions of the present invention may also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2, preferably up to 1 % by weight of the total composition.

Among suitable hair care adjuvants, are natural hair root nutrients, such as amino acids and sugars. Examples of suitable amino acids include arginine, cysteine, glutamine, glutamic acid, isoleucine, leucine, methionine, serine and valine, and/or precursors and derivatives thereof. The amino acids may be added singly, in mixtures, or in the form



of peptides, e.g. di- and tripeptides. The amino acids may also be added in the form of a protein hydrolysate, such as a keratin or collagen hydrolysate. Suitable sugars are glucose, dextrose and fructose. These may be added singly or in the form of, e.g. fruit extracts. A particularly preferred combination of natural hair root nutrients for inclusion in compositions of the invention is isoleucine and glucose. A particularly preferred amino acid nutrient is arginine. Another suitable adjuvant is glycolic acid.

#### Optional Ingredients

Compositions of this invention may contain any other ingredient normally used in hair treatment formulations.

These other ingredients may include viscosity modifiers, preservatives, colouring agents, polyols such as glycerine and polypropylene glycol, chelating agents such as EDTA, antioxidants, fragrances, antimicrobials and sunscreens. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally these optional ingredients are included individually at a level of up to 5% by weight of the total composition.

#### Mousses

Hair treatment cleansing and conditioning compositions in accordance with the invention may also take the form of aerosol foams (mousses) in which case a propellant is included in the composition. This agent is responsible for expelling the other materials from the container and forming the hair mousse character.

The propellant gas can be any liquefiable gas conventionally used for aerosol containers. Examples of suitable propellants include dimethyl ether, propane, n-butane and isobutane, used singly or in admixture.

5

The amount of the propellant gases is governed by normal factors well known in the aerosol art. For hair mousses, the level of propellant is generally from 3 to 30, preferably from 5 to 15 % by weight of the total

10

composition.

#### Mode of Use

15

The compositions of the invention are primarily intended for topical application to the hair and/or scalp and or skin of a human subject as rinse-off treatments to clean the hair or body while improving hair fibre surface properties such as smoothness, softness, manageability, cuticle integrity, and shine. Typically such compositions are known in the art as

20

shampoos, cleansing mousses or shower gels.

25

In particular, compositions according to the invention are used for improving the deposition of silicone conditioning oil onto the tip region of hair relative to the root region of hair.

30

Thus one aspect of the invention comprises a method of cleaning and conditioning hair by applying compositions according to the invention followed by rinsing.

---

The invention is further demonstrated with reference to the following, non-limiting examples:

### Examples

5

Example 1 is according to the invention. Examples A B and C are comparative examples.

Table 1

10

Ingredient	Trade Name	Supplier	Example A weight %	Examples B,C and 1 weight %
Sodium laureth (2 EO) sulphate	Empicol ESB70	Albright & Wilson	16	16
Coco amidopropyl betaine	Tegobetaine CK	Goldschmidt	2	2
PDMS fluid (60,000 mm <sup>2</sup> sec <sup>-1</sup> )	DC200	Dow Corning	1	1
block copolymer	Various (see table 2)		-	0.05
Sodium Chloride	Salt	BDH	1	1
Water	-	-	To 100	To 100

Compositions in table 1 were prepared as described above by forming an aqueous emulsion of the DC200 using a suitable nonionic emulsifier and the block copolymer (when present as indicated in the table). The subsequent emulsion was then blended with the other ingredients except salt. The salt was finally added to thicken the composition.

### Test Method

0.25g/5 cm switches of tip hair which had been cleaned with a solution of 14% SLES 2EO and 2% cocoamidopropyl betaine in water followed by extensive rinsing, were used for this experiment. The test shampoo was diluted to 1 in 10 by weight with distilled water and stirred throughout with a magnetic stirrer. 5 switches were placed in one half of a petri dish. 1.5 mls of diluted shampoo was placed along the length of the switches which were then agitated in the dish for 30 seconds, followed by a rinse for 30 seconds under tap water (12° French hard) at 40°C, with a flow rate set at 3-4 litres per minute. The washing process using the test shampoo solution was repeated followed again by rinsing. The switches were then allowed to dry naturally at 25° C and a relative humidity of 45 to 60%.

The same sequence of experimentation was carried out for 0.25g/5 cm samples of root hair.

The amount of silicone deposited on the hair samples was measured using X-ray fluorescence spectrometry (measured in parts per million (ppm) of silicon).

### 25 Analysis results

The absolute selectivity expressed as a percentage is the ratio of silicon ppm on the tip samples to silicon ppm on the root samples multiplied by 100.

The absolute selectivity calculated for Example A (without block copolymer) was then subtracted from the absolute selectivity calculated for each of the other Example formulations to derive a targeting score. The results are shown below in Table 2. A targeting score of 5% or less is considered to be of no significant value.

Table 2

Example	Polymeric emulsifier	m	n	Molecular Weight	Targeting score(%)
A	None (DC200 benchmark)	-	-	-	0
B	ABA silicone polyether (12EO)	12	13	2000	4
C	Rake silicone polyether	-	-	-	2
1	ABA silicone polyether (40EO)	40	13	4500	16

The silicone polyethers are experimental materials supplied by Dow Corning.

Example C is a rake copolymer with EO side chains attached to a polydimethylsiloxane backbone. The results show that this molecular architecture does not provide targeting in this formulation.

- 27 -

Examples B and 1 are ABA block copolymers according to formula I. Both have  $n=13$ . Example B has  $m=12$  while example 1 has  $m=40$ . The results show significant targeting of silicone to the hair tip for example 1 and not for comparative example B.

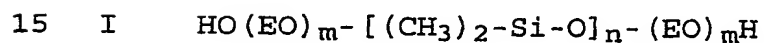
5

---

CLAIMS

1. An aqueous hair conditioning composition comprising;

- 5 a) from 1% to 50% by weight of a cleansing surfactant,
- b) discrete, dispersed droplets comprising a water insoluble silicone conditioning oil, characterised in that the mean diameter of the droplets ( $D_{3,2}$ ) is
- 10 from 2 to 100 micrometres and
- c) a surface active block copolymer according to formula I:



wherein m is 30 or more, n is 5 or more and the ratio n/m is from 0.1 to 1.2.

20 2. A composition according to claim 1 comprising from 0.01% to 0.4% by weight of surface active block copolymer.

3. A composition according to any preceding claim wherein the silicone conditioning oil has a viscosity from 5000 to

25  $1000000 \text{ mm}^2 \text{ sec}^{-1}$  at 25° C.

4. A composition according to any preceding claim wherein the silicone oil comprises a functionalised silicone.

---

5. A composition according to claim 4 wherein the functionalised silicone is a silicone copolyol with an HLB of 10 or less.

5 6. A composition according to claim 4, wherein the functionalised silicone is an amino-functionalised silicone.

10 7. A composition according to claim 6 wherein the amino-functionalised silicone has a weight percent amino functionality from 0.03 to 8, preferably from 0.5 to 4 percent.

15 8. A composition according to any preceding claim wherein the composition comprises less than 0.01% by weight of a cationic deposition polymer.

20 9. A composition according to any preceding claim wherein the cleansing surfactant is selected from the group consisting of anionic, amphoteric, zwitterionic and nonionic surfactants and mixtures thereof.

10. A method for preparing an aqueous hair conditioning composition according to any preceding claim comprising the steps of:

25

i) preparing a solution comprising water and the surface active block copolymer,

ii) adding a silicone conditioning oil to the solution,

30



- 30 -

iii) forming the solution and the silicone conditioning oil into an oil-in-water emulsion by high-shear mixing,

5      iv) dispersing the oil-in-water emulsion comprising the block copolymer into a hair conditioning composition.

11. A method for preparing a hair conditioning composition  
10 according to claim 1 comprising the steps of:

i) preparing an oil-in-water emulsion of a silicone conditioning oil,

15      ii) dispersing the surface active block copolymer into the emulsion,

20      iii) dispersing the oil-in-water emulsion comprising the block copolymer into a hair conditioning composition.

12. The use of a composition according to any one of claims 1 to 9 for cleaning and conditioning hair.

---

- 31 -

13. A method of cleaning and conditioning hair by applying a composition according to any one of claims 1 to 9 followed by rinsing.

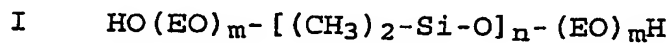
5 14. The use of a composition according to any of claims 1 to 9 for improving the deposition of silicone conditioning oil onto the tip region of hair relative to the root region of hair.

---

ABSTRACT

Aqueous hair conditioning compositions comprising; a) from 1% to 50% by weight of a cleansing surfactant, b) discrete, dispersed droplets comprising a water insoluble silicone conditioning oil, characterised in that the mean diameter of the droplets ( $D_{3,2}$ ) is in the range from 2 to 100 micrometres and c) a surface active block copolymer according to formula I:

10



wherein m is 30 or more, n is 5 or more and the ratio n/m is from 0.1 to 1.2.

PCT Application

**EP0312220**



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**